



Short communication

## Stability of nanostructured iridium oxide electrocatalysts during oxygen evolution reaction in acidic environment



Serhiy Cherevko<sup>a,1</sup>, Tobias Reier<sup>b,1</sup>, Aleksandar R. Zeradjanin<sup>a</sup>, Zarina Pawolek<sup>b</sup>, Peter Strasser<sup>b,\*</sup>, Karl J.J. Mayrhofer<sup>a,\*</sup>

<sup>a</sup> Department of Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

<sup>b</sup> Department of Chemistry, Technical University Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

### ARTICLE INFO

#### Article history:

Received 29 July 2014

Received in revised form 27 August 2014

Accepted 27 August 2014

Available online 6 September 2014

#### Keywords:

Oxygen evolution

Energy conversion

Iridium oxide

IrO<sub>2</sub>

Dissolution

Corrosion

### ABSTRACT

The electrochemical stability of thermally prepared Ir oxide films is investigated using a scanning flow cell (SFC)–inductively coupled plasma mass-spectrometer (ICP-MS) setup under transient and stationary potential and/or current conditions. Time-resolved dissolution rates provide important insights into critical conditions for material breakdown and a fully quantitative in-situ assessment of the electrochemical stability during oxygen evolution reaction (OER) conditions. In particular, the results demonstrate that stability and OER activity of the IrO<sub>x</sub> catalysts strongly depend on the chemical and structural nature of Ir oxide species and their synthesis conditions.

© 2014 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

## 1. Introduction

Iridium oxide is a benchmark material for the (photo)-electrocatalytic oxygen evolution reaction (OER) in acidic media. Consequently, literature on the OER on Ir oxide is extensive [1–22]. Ir oxide species are usually divided into two categories, a highly defective amorphous and an anhydrous crystalline. It has been suggested repeatedly that the electrochemically prepared hydrated amorphous Ir oxide has a very high OER activity but suffers from severe corrosion [23–27]. Stabilization of hydrated amorphous Ir oxide can be achieved by heat treatment [28], therefore, the degree of hydration is supposed to be one important parameter for oxide stability [1]. Crystalline, anhydrous Ir oxide is believed to be more stable but less active for the OER and is a key component of industrially employed Dimensionally Stable Anodes (DSA) in electrolysis technology [29–31]. On the other hand, amorphous oxides are prone to corrosion during OER [20]. Interpretation of the experimental results obtained from such systems is however complicated, due to the complex mass transport and interactions between electrode components in a reactor. Recently, we presented a detailed study of how thermal treatment of IrO<sub>x</sub> thin-film catalysts influences the OER

kinetics [32–34]. What has remained unaddressed to date, however, concerns the correlation between geometric and electronic structure of the Ir oxide films and their electrochemical stability. This is the focus of the present study.

In the current work metallic iridium and thermally prepared iridium oxide thin-film model catalysts (on Ti substrates), fully characterized in terms of material properties and OER activity [32,33], are investigated using a scanning flow cell inductively coupled plasma mass spectrometry (SFC-ICP-MS) setup [35,36], and compared in terms of dissolution at conditions relevant to the OER.

## 2. Experimental

Thin iridium oxide films were prepared by spin coating of an Ir acetate precursor (thermally decomposable in air at 250 °C) on a Ti substrate and subsequent calcination in air according to [32,33]. Dissolution of metallic iridium was investigated on a polycrystalline Ir disk (MaTeck, Germany). All electrochemical and spectrometric measurements were performed using an SFC coupled with an ICP-MS (NexION 300X, Perkin Elmer) as described elsewhere [35,37,38]. The measurements were performed at room temperature applying 0.1 M perchloric acid (Merck Suprapur® 70% HClO<sub>4</sub> diluted using ultrapure water (PureLab Plus system, Elga, 18 MΩ, TOC < 3 ppb)) as electrolyte.

\* Corresponding authors.

E-mail addresses: [pstrasser@tu-berlin.de](mailto:pstrasser@tu-berlin.de) (P. Strasser), [mayrhofer@mpie.de](mailto:mayrhofer@mpie.de) (K.J.J. Mayrhofer).

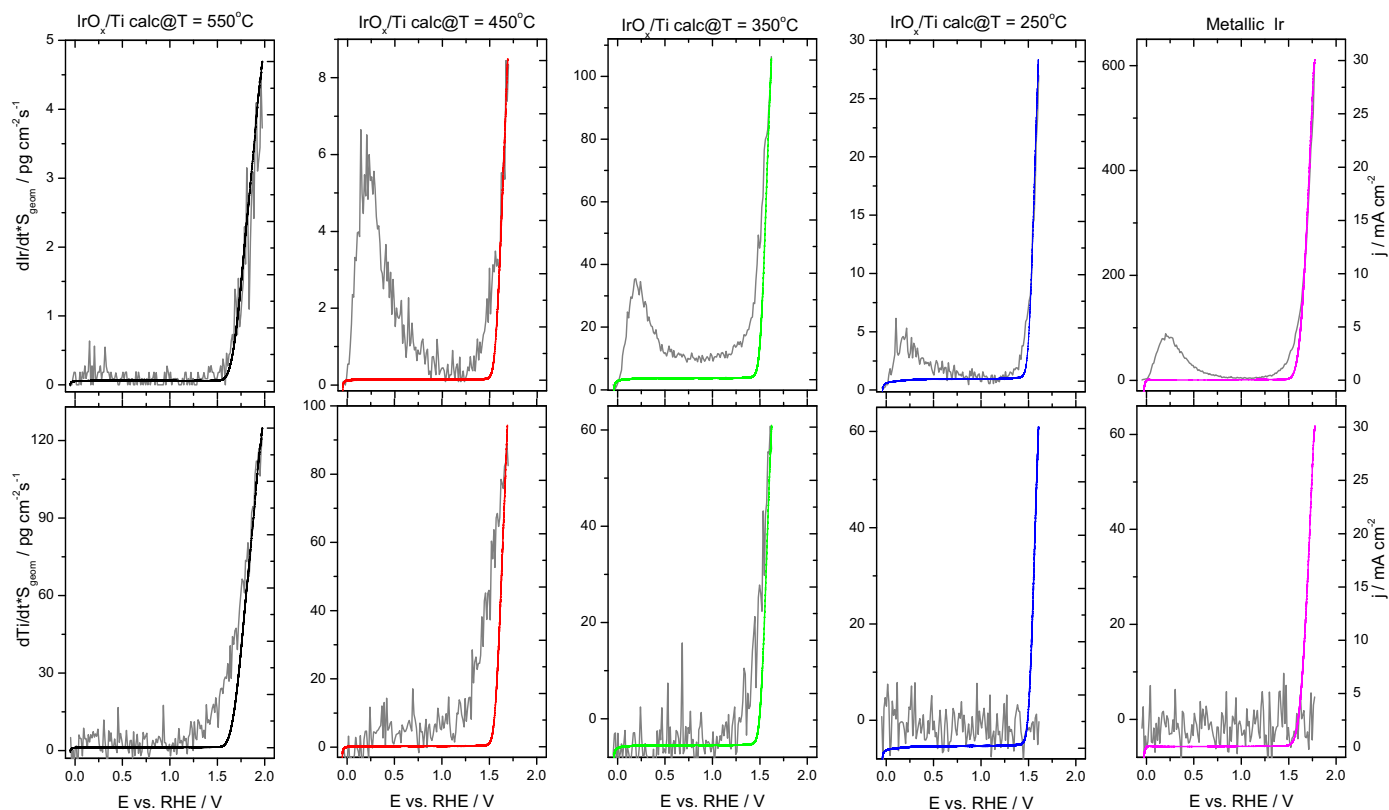
<sup>1</sup> These authors contributed equally to this work.

### 3. Results and discussion

Initial stability screening was performed by applying an electrode potential ramp starting at  $E = -0.05 V_{\text{RHE}}$  and ending at the potential where a current density  $j = 30 \text{ mA cm}^{-2}$  was reached. Corresponding real-time dissolution profiles of Ir and Ti are shown in Fig. 1. Note that for clarity the scaling of the y-axis is different in each partial plot. As can be clearly seen from the graphs in Fig. 1, all samples except  $\text{IrO}_x@550^\circ\text{C}$  (here and below the numeric value represents the calcination temperature), start to dissolve already at low potentials. On the other hand no measurable amount of Ir was detected in the electrolyte when the ramp was started from open circuit potential (OCP ca.  $0.9\text{--}1.0 V_{\text{RHE}}$ ). Thus, we attribute this dissolution process to cathodic transient dissolution [38,39]. In terms of the amount of cathodically dissolved material,  $\text{IrO}_x@350^\circ\text{C}$  is the least stable oxide. Surprisingly, the highest dissolution peak was found on metallic Ir, which is most likely due to the reduction of the innate surface oxide formed in air. In this potential region no Ti dissolution was detected. The initial cathodic Ir dissolution decreased as the potential was swept anodically. Data in Fig. 1 evidences that at and above electrode potentials where the OER is thermodynamically possible, Ir dissolution initiates.  $\text{IrO}_x@550^\circ\text{C}$  exhibits the highest Ir dissolution and OER onset potential of  $E = 1.5 V_{\text{RHE}}$ . The dissolution rate measured at  $j = 30 \text{ mA cm}^{-2}$  was used for a quantitative comparison of catalyst dissolution during the OER (see Table 1 below).  $\text{IrO}_x@550^\circ\text{C}$  is the most stable, while metallic Ir was found to be the least stable of all electrode materials investigated. The increased stability of the  $\text{IrO}_x@450^\circ\text{C}$  compared to the films calcined at 250 and 350 °C is likely correlated with the formation of a crystalline  $\text{IrO}_2$  phase at 450 °C that was shown to exhibit a higher degree of lattice oxygen at the surface and consequently a lower

degree of surface hydroxylation [32,33]. It seems plausible to conclude that crystalline order and lattice oxygen at the surface stabilize the Ir oxide against corrosion. At 550 °C calcination temperature, Ti diffuses into the Ir oxide layer and alters its chemical properties [32,33], which seem to result in further stabilization. Interestingly, the fully amorphous  $\text{IrO}_x@250^\circ\text{C}$  is by a factor of 4 more stable than the oxide film calcined at 350 °C, which is comprised of a mixture of the crystalline and the amorphous Ir oxide species. To explain the enhanced corrosion of the 350 °C film electrode, we therefore put forward the hypothesis that the coexistence of an amorphous and a crystalline phase is conducive to enhanced metal dissolution from the amorphous phase combined with metal ion transport, possibly at and along grain boundaries. In parallel to Ir, Ti dissolution was observed for all samples except for  $\text{IrO}_x@250^\circ\text{C}$  and metallic Ir, with a clear trend of increasing Ti dissolution with increase in the calcination temperature.

The operation of water electrolyzers powered by renewable energy is expected to be intermittent, which may pose additional issues for catalyst stability [40,41]. To simulate fluctuating power inputs on the stability of the catalysts, consecutive square wave cycles with loads of  $j = 5 \text{ mA cm}^{-2}$  over 3 s and idle breaks of  $j = 0 \text{ mA cm}^{-2}$  over 3 s were applied. Corresponding dissolution profiles for Ir and Ti are shown in Fig. 2a and b, respectively, and the results are in line with those presented in Fig. 1. In particular, among all calcined Ir oxides  $\text{IrO}_x@350^\circ\text{C}$  was the least stable. Again, dissolution of Ti was observed on all calcined electrodes except  $\text{IrO}_x@250^\circ\text{C}$ . The amount of dissolved Ti for the three samples was similar. In the studied time interval dissolution of both metals did not reach a steady state value, although it is still possible to estimate dissolution tendency. At the end of the measurement, dissolution from the samples calcined at 450 °C and 550 °C was below the experimental detection limit of  $0.5 \text{ pg cm}^{-2} \text{ s}^{-1}$  and  $15 \text{ pg cm}^{-2} \text{ s}^{-1}$  ( $S/N = 3$ ) for Ir and Ti, respectively. Initial Ir dissolution



**Fig. 1.** Mass-spectrometric linear voltammograms (gray lines) and electrochemical linear voltammograms (colored lines) taken from four Ir oxide samples calcined at different temperatures and metallic Ir as indicated in the figure. Dissolution of Ir and Ti is presented in top and bottom row images, respectively. The potential was scanned from  $-0.05 V_{\text{RHE}}$  to a potential corresponding to current density of  $j = 30 \text{ mA cm}^{-2}$  at which the scan was stopped and OCP was established. The scan rate was  $10 \text{ mV s}^{-1}$ .

Download English Version:

<https://daneshyari.com/en/article/6601396>

Download Persian Version:

<https://daneshyari.com/article/6601396>

[Daneshyari.com](https://daneshyari.com)